

PRV

PATENT- OCH REGISTRERINGSVERKET
Patentavdelningen

Rec'd PCT/PTC 11 APR 2005
PCT/ SE 0 3 / 0 1 5 7 1

Intyg Certificate

Härmed intygas att bifogade kopior överensstämmer med de handlingar som ursprungligen ingivits till Patent- och registreringsverket i nedannämnda ansökan.

This is to certify that the annexed is a true copy of the documents as originally filed with the Patent- and Registration Office in connection with the following patent application.



(71) Sökande Institutet för Metallforskning AB, Stockholm SE
Applicant (s)

(21) Patentansökningsnummer 0203038-5
Patent application number

(86) Ingivningsdatum 2002-10-11
Date of filing

REC'D 24 OCT 2003

WIPO PCT

Stockholm, 2003-10-14

För Patent- och registreringsverket
For the Patent- and Registration Office

Lisa Junegren
Lisa Junegren

Avgift
Fee

CERTIFIED COPY OF
PRIORITY DOCUMENT

PRIORITY DOCUMENT
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH
RULE 17.1(a) OR (b)

Process and plant for manufacturing fine iron and steel powders, fine iron and steel powders and use of powders manufactured by the process

BACKGROUND OF THE INVENTION

5

1. Field of the invention

The present invention relates to a process for manufacturing fine iron and steel powders.

10

The present invention further relates to a plant for manufacturing fine iron and steel powders.

15

The present invention also relates to fine iron and steel powders as well as use of powders manufactured by the process according to the invention.

2. Description of the related art

20

Fine iron and steel powders, mean particle sizes being from 1-50 μm , are expensive due to, inter alia, the manufacturing processes employed. Thus, it is known to use an atomizing process, which calls for inert gas as protection, the cost increasing steeply with decreasing particle size etc. Further it is known to use finely divided iron oxide, which is reduced to iron, this process, however, being limited, by, inter alia, sintering. Further a process called the carbonyl process employing gaseous reactants is known, the process, however, calling for rigorous safety and environmental considerations, due to the toxic substances employed.

25

30

One of the basic problems and the reasons for using the processes described above is the fact that milling of an iron or steel fragmented raw material does not provide the possibility of further dividing raw materials of a certain grain size due to the fact that deformation instead of crushing of the quite ductile grains occur.

The present invention offers a solution to these problems and provides a comparatively inexpensive way of manufacturing fine iron and steel powders.

5 SUMMARY OF THE INVENTION

Thus, the present invention relates to a process according to the introductory part of the accompanying claim 1. The process is especially characterized in what is specified in the characterizing portion of said claim.

10

Further, the present invention relates to a plant according to the introductory part of the accompanying claim 15. The plant is especially characterized in what is specified in the characterizing portion of claim 15.

15

The invention further relates to a fine iron or steel powder according to the introductory part of the accompanying claim 29. The powder is especially characterized in what is specified in the characterizing portion of claim 29.

Furthermore the invention relates to use of powder as specified in claims 26 - 28.

20

BRIEF DESCRIPTION OF THE DRAWINGS

In the following the invention is described in more detail in connection with exemplifying embodiments and the accompanying drawings, in which

25

Fig. 1 schematically shows different embodiments of the process according to the invention and

Fig. 2 shows porosity in a steel material sintered from powder produced according to the invention as an alloying substance.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

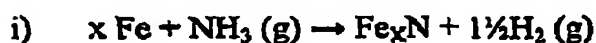
In Fig. 1, a raw material preparation step is designated by 1. Fragmented raw materials according to the invention are, primarily and preferably, taken from the following groups:

- 1) finely divided iron (eg iron powder) or porous iron (eg sponge iron)
- 2) fine iron oxide powder, and
- 3) finely divided steel (eg steel powder or turning scrap)

"Finely" and "fine" as far as the fragmented raw materials are concerned is intended to cover a wide range of particle sizes, such as 50 - 500 μm , the sizes, however, not being limited to these sizes. Porous iron, eg sponge, does not have to be as finely divided as iron powder since a large contact area for gas is provided due to the pores. Further, iron oxide powder is normally provided in the form of fine powder as a raw material, which means that milling of the iron oxide in the present process may be unnecessary.

The raw material may be taken from one or more of these groups, a mixture of different raw materials being possible to use.

2 designates a nitriding step in which raw material is intended to be transformed substantially totally to nitride by means of ammonia gas, eg according to the reaction i):



Nitriding transforms, mainly, the iron of the raw material to a brittle nitride material, a possible nitrogen content being about 3 - 20% by weight, a preferred

nitrogen content being above 6% by weight. In the following, contents are given as percentage by weight.

5 The nitriding operation is performed in eg a standard rotating tube furnace, not shown, in which a stream of ammonia gas is conveyed through or above the raw material, the operation taking place at about 400 -800 °C, preferably at about 500 - 700 °C.

10 The brittle nitride is, when applicable, intended to be crushed to the desired particle sizes in a milling operation 3, the milling means provided being of a kind known per se and not shown, eg ball milling equipment or jet milling equipment for milling materials down to micron sizes.

15 The milling means may be arranged for batchwise or continuous milling.

Further, the transformation to nitride and milling may be performed in an integrated process step comprising both nitriding and milling. This is schematically shown in Fig. 1 by the dashed frame 5 enclosing steps 2 and 3. This integrated step may be performed in eg a rotating tube furnace, not shown, provided with milling bodies during said transformation.

20 According to preferred embodiments separation means are provided for a separation step 6 for obtaining a fraction of powder particles within a desired particle size interval. For this eg existing sieving or elutriation techniques and equipments, not shown, may be used.

25 According to one embodiment transformation, milling and particle size separation are arranged in an integrated process step arrangement in which at least too coarse particles are intended to be recirculated from the separation operation 4 to the transformation operation 2 as schematically shown by means of the arrow 7 in Fig.

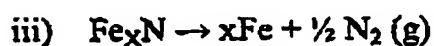
Since the time necessary for total nitriding of raw material particles increases quite rapidly with increasing particle size, one embodiment of the process might be to nitride an outer shell of particles with considerable size, since nitriding takes place from the outside, and to mill such particles so that said outer shell, which is brittle, is crushed off and to recirculate the remaining raw material core for further nitriding, milling etc. This will in certain cases improve the productivity. If nitriding and milling is integrated, such an operation will be performed automatically.

10 In Fig. 1, 8 designates a denitriding step, in which a fine powder from the former steps is retransformed, preferably by means of hydrogen gas, according to the reaction, ii):



15 by means of which metallic iron of the powder and ammonia gas are regenerated. This reaction is best utilized by means of arrangements for conveying a stream of hydrogen gas through and/or above the processed powder, eg in a tube furnace, not shown, at temperatures about 250 – 400 °C, preferably about 300 – 350 °C.

20 Denitriding may also be performed according to the reaction, iii):



25 at temperatures about 500 – 700 °C and by using gasses like nitrogen or argon or by vacuum pumping.

The hydrogen treatment is normally preferred since it also leads to the reduction of iron oxides and allows comparatively low temperatures in order to minimise agglomeration of the resulting powder. Thus, there happens to be almost no agglomeration at all at temperatures below about 350 °C.

30

Example 1.

- 8 kilograms of an iron powder ($d_{89} = 300 \mu\text{m}$, 0,66 % O and 0,042 % C) was
5 nitrided during 34 hours using a flow of 3 litres NH_3 per minute at 525 °C. An
analyses showed that the nitrided powder had a nitrogen content of about 7 %.

Example 2.

- 10 600 grams of nitrided iron powder from Example 1 was milled by jet milling
technique by means of a laboratory jet mill to a fine powder with $d_{50} = 3 \mu\text{m}$.
Milling of another nitrided powder (nitrided tool steel) by means of the laboratory
jet mill revealed that the productivity is a function of the mean particle size of the
milled material:
15 0,1 kilogram per hour for $d_{50} = 3 \mu\text{m}$ and 3,2 kilogram per hour for $d_{50} = 20 \mu\text{m}$,
respectively.

Example 3.

- 20 0,8 grams iron nitride (7 % N and 1,4 % O) with $d_{50} = 3 \mu\text{m}$ was filled into a cup
with $\varnothing = 4$ millimetres to a bed depth = 7 millimetres. After a treatment at 300 °C
using a flow of 50 millilitres H_2 (g) per minute in 90 minutes the material was still a
fine powder, i e no agglomeration occurred. The powder was not pyrophoric after
the treatment. An analyses of the powder showed that it contained 0,28 % N and
25 0,74 % O.

Example 4.

Finely milled iron nitride with d_{50} = about 10 μm was mixed with a somewhat coarser master alloying powder of a stainless composition (316L/MA: 38 % Ni, 7,2 % Mo, 1,0 % Si, 0,5 % Mn, bal. Cr) to a mixture ratio of 68,9/31,1. The mixture was heated in hydrogen gas to sintering temperature, 1300 °C, the holding time being 60 minutes. The sintered samples were analysed chemically and metallographically. The chemical analysis showed that the remaining content of nitrogen was below 150 ppm and of oxygen below 300 ppm. The metallographic study showed that a closed porosity had been achieved. The pore size was below 5 μm and the volume fraction of pores was below 1 %, Fig. 2. Thus, the results show that finely milled iron nitride powder can replace carbonyl iron powder as a sintering active powder for the production of high alloy steel components.

15

The process according to the present invention as well as the function of the plant according to the present invention should to the extent necessary be obvious from the above description.

20

Thus, iron or steel fragmented raw material, preferably finely divided iron, porous iron, fine iron oxide or finely divided steel, is nitrided by ammonia gas in order to obtain a brittle material suitable for milling. The material thus transformed is, when applicable, milled, preferably separated with respect to particle sizes and then denitrided, whereby the iron based nitridic material is totally or substantially totally denitrided to form a fine iron or steel powder, the iron powder in certain cases still comprising a certain amount of remaining iron nitride and the steel powder in certain cases still comprising certain metal nitrides, as discussed later. Further, fine iron or steel powders thus produced may to a certain extent contain normal impurities and the terms iron powder and steel powder are here intended to also cover powders containing such impurities.

25

30

The particle size distribution is controlled by the operating parameters of the milling process. Mean typical particle sizes produced are about 1 – 50 μm , often preferred sizes being about 3 – 25 μm . The particles are not spherical, but a large fraction of the particles possess a more or less equiaxed morphology. TAP densities above
5 4g/cm^3 can be reached for powders not much finer than a $d_{50} = 10 \mu\text{m}$.

By using raw materials within the groups 1 and 2, a pure iron powder is produced according to the invention. This product can be used for various sintering applications, particularly those which demands powders with high sintering activity,
10 eg metal injection molding. However, a large area of applications can be found in the food and medical industry, as iron additives. Other areas of applications are in various magnetic applications.

Raw materials from group 3 results in a steel powder with maintained material
15 composition except for the nitrogen still remaining after denitridation in compounds with alloying elements such as molybdenum and chromium, i.e. in nitrides more stable than iron nitride. The product is intended to be used in various sintering applications, particularly those which demands powders with high sintering activity, e.g. metal injection molding. In such applications nitrides of molybdenum and
20 chromium will loose its nitrogen (spontaneous denitridation) during heating to sintering temperatures (e.g. chromium nitride decomposes to chromium and nitrogen gas at temperatures exceeding about 1050 °C). However, this is only possible if the produced nitrogen gas is allowed to escape from the porous presintered body by a flowing process gas or by vacuum pumping (e.g. in the
25 process of sintering metal injected parts). Consequently, the nitrogen content of the finally sintered part may be reduced to very low levels (e.g. less than 200 ppm) if necessary, even in the case of a stainless steel composition. In comparison to conventional powders prepared by atomization, used for example in metal injection molding, the main advantage of this product is a low cost for its preparation and a
30 high freedom of controlling particle size distribution.

Above the invention has been described in connection with preferred embodiments.

Of course further embodiments as well as minor changes and additions may be imagined without deserting the basic inventive idea.

5

Thus, when applicable, milling and separation may be performed dry or wet. However, after wet milling and separation the finely milled product has to be dried (dehydrization, vacuum drying, etc), eventually followed by a deagglomeration step.

10

As mentioned before nitriding and/or denitriding may be performed in a, preferably rotating, tube furnace but may also be performed in e.g. a belt furnace, gas preferably being provided in a counter flow arrangement in relation to the powder flow, i.e. the belt movement in the furnace. Further, a fluidized bed arrangement may be used, the powder being the bed material.

15

Thus, the invention should not be considered to be limited to the embodiments described but may be varied within the scope of the accompanying claims.

20

11
12
13
14
15
16
17
18
19
20
21
22
23
24
25

Claims

1. Process for manufacturing fine iron or steel powders, characterized in the steps of

- providing an iron based, fragmented raw material, finely divided when applicable,
- providing a brittle material by transforming raw material to nitride by means of ammonia gas,
- milling the nitridic material to particle sizes desired, when applicable, and
- denitriding to a fine iron or steel powder.

2. Process according to claim 1, characterized in that the raw material is chosen from one or more of the material groups

- 1) iron, eg iron powder and/or sponge iron
- 2) iron oxide powder

3) steel, eg steel powder and/or turning scrap.

3. Process according to claim 1 or 2 characterized in that the transformation to nitride is carried out at 400 – 800 °C, preferably at 500 – 700 °C.

4. Process according to claim 1, 2, or 3, characterized in that the nitrogen content is about 3 – 20 % by weight, preferably more than 6 % by weight.

5. Process according to anyone of the preceeding claims, characterized in that milling (3) is performed by means of milling equipment know per se, eg ball milling equipment or jet milling equipment, for milling materials down to micron sizes.

6. Process according to anyone of the preceeding claims, characterized in that milling is performed batchwise or continuously.

7. Process according to anyone of the preceeding claims, characterized in that a fraction of powder particles within a desired particle size interval is obtained by separation, eg by sieving or elutriation techniques in a batchwise or continuous separation procedure (6).

8. Process according to claim 7, characterized in that milling and separation is performed dry or wet.

9. Process according to anyone of the preceeding claims, characterized in that transformation to nitride (2), milling and particle size separation is performed in an integrated process in which too coarse, separated particles are recirculated from the separation step to the transformation step.

5 10. Process according to anyone of the preceeding claims, characterized in that transformation to nitride and milling is performed in an integrated process step (4), eg by providing milling bodies during the transformation in a rotating tube furnace.

10 11. Process according to anyone of the preceeding claims, characterized in that denitridding is performed by means of hydrogen gas.

12. Process according to claim 11, characterized in that denitridding is performed at 250 – 400 °C, preferably at 300 – 350 °C.

13. Process according to anyone of the preceeding claims, characterized in that nitride powder is produced as an alloying substance for sintering purposes.

15 14. Process according to anyone of the preceeding claims, characterized in that mean particle sizes of the produced powders are about 1 – 50 µm, preferably about 3 – 25 µm.

15. Plant for manufacturing fine iron or steel powders, characterized by

- 20
- means (2) for containing a fragmented iron based raw material,
 - means for providing ammonia gas to said raw material for transforming iron of the raw material substantially totally to nitride,
 - milling means (3), when applicable, for milling the nitridic material to particle sizes desired and
 - means (8) for denitridding to a fine iron or steel powder.

25 16. Plant according to claim 15, characterized in that said transformation is intended to occur at about 400 – 800 °C, preferably at about 500 – 700 °C.

17. Plant according to claim 15 or 16, characterized in that said transformation is intended to provide a nitrogen content of about 3 – 20 % by weight, preferably over 6 % by weight.

18. Plant according to claim 15, 16 or 17, characterized in that said milling means is milling equipment of a kind known per se, eg ball milling equipment or jet milling equipment for milling materials down to micron sizes.

19. Plant according to claim 15, 16, 17 or 18, characterized in that the milling means are arranged for batchwise or continuous milling.

20. Plant according to claim any of claims 15 - 19, characterized by separation means for obtaining a fraction of powder particles within a desired particle size interval, eg sieving or elutriation means, said separation means being arranged for batchwise or continuous operation.

21. Plant according to any of claims 15 - 20, characterized in that milling and separation is intended to be performed dry or wet.

22. Plant according to anyone of claims 15 - 21, characterized in that transformation to nitride, milling and particle size separation is intended to be performed in an integrated process arrangement in which too coarse particles are arranged to be recirculated from a separation operation to a transformation operation.

23. Plant according to anyone of claims 15 - 22, characterized by an integrated process step for transformation to nitride and milling, eg a rotating tube furnace provided with milling bodies, during transformation.

24. Plant according to anyone of claims 15 - 23, characterized by arrangements for providing hydrogen gas for denitrifying the nitride powder.

25. Plant according to anyone of claims 15 - 24, characterized in that denitrifying is intended to be performed at about 250 - 400 °C, preferably about 300 - 350 °C.

26. Use of fine iron based nitride powder according to anyone of claims 1 - 14 as an alloying substance in sintered steel production.

27. Use according to claim 25, characterized in that mean particle sizes of the powders are about 1 - 50 µm, preferably about 3 - 25 µm.

28. Use of fine iron or steel powder according to anyone of claims 1 - 14 as material for metal injection moulding (MIM).

29. Fine iron or steel powder characterised in that it is produced by the process according to anyone of claims 1 - 14.

ABSTRACT

Process for manufacturing fine iron or steel powders.

- 5 **The process is especially characterized in the steps of**
- **providing an iron based, fragmented raw material, finely divided when applicable,**
 - **providing a brittle material by transforming raw material to nitride by means of ammonia gas,**
 - 10 • **milling the nitridic material to particle sizes desired, when applicable, and**
 - **denitridding to a fine iron or steel powder.**

15 **The invention also relates to a plant for manufacturing fine iron or steel powders, fine iron or steel powders and use of powders manufactured by the process according to the invention.**

(Fig. 1)

11/10/2002
13/88
ALBIHNS STOCKHOLM AB → 64560286
08 59887300
NR. 250
13
ABSTRACT
Process for manufacturing fine iron or steel powders.
5 The process is especially characterized in the steps of
• providing an iron based, fragmented raw material, finely divided when applicable,
• providing a brittle material by transforming raw material to nitride by means of ammonia gas,
10 • milling the nitridic material to particle sizes desired, when applicable, and
• denitridding to a fine iron or steel powder.
The invention also relates to a plant for manufacturing fine iron or steel powders, fine iron or steel powders and use of powders manufactured by the process according to the invention.
15
(Fig. 1)

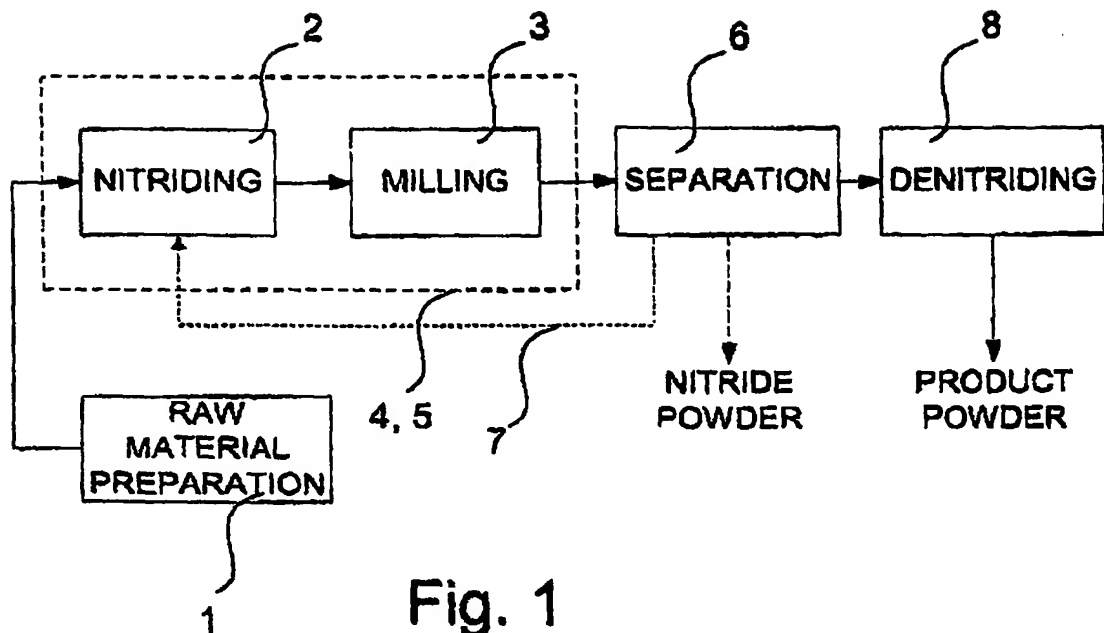


Fig. 1

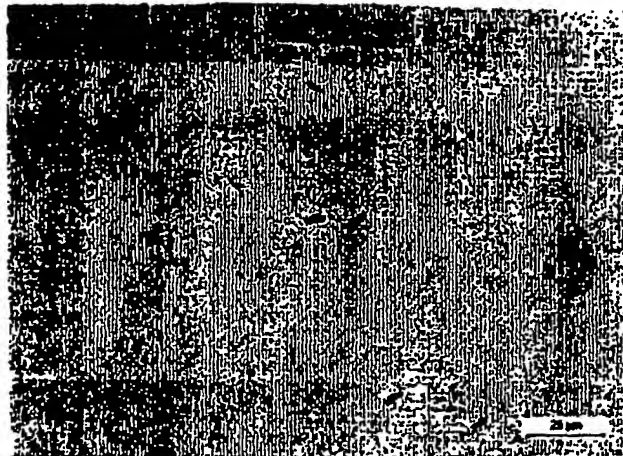


Fig. 2